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TOXICITY AND BIODEGRADABILITY OF DARLINGTON FEEDER HEADER ASSEMBLY CLEANING WASTES

Report No. 86-44-K

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ABSTRACT

Wastewater from cleaning heavy equipment requires disposal, but its effect on a potential receiving area, the Wesleyville sewage lagoon, must be assessed prior to discharge. The toxicity and biodegradability of dilute and concentrated waste in contact with the lagoon microbial population present in the summer were evaluated, chemical and physical parameters measured and the results compared with a previous study performed under winter conditions. The summer population was less sensitive to toxicity and capable of greater waste biodegradation than the winter population, results which were further enhanced by prolonged incubation and aeration indicating that a disposal strategy should include waste storage, dilution and aeration. Concentrations of six heavy metals, aluminum, suspended and dissolved solids were in excess of regulatory guidelines and although dilution would remove this problem the presence of mercury, which bioaccumulates, is of concern.

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EXECUTIVE SUMMARY

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Wastewater from the Feeder Header Assembly (FHA), for use at Darlington NGS, is currently being stored in a neutralization pond at Wesleyville GS. The aim of this phase is to provide recommendations for disposal of dilute FHA cleaning waste stored in a neutralization pond and for future batches of concentrated FHA Wash.

Three sets of serial dilutions of the two types of FHA Wash were exposed to the microbial population present in the sewage lagoons during the summer months. One set was left in contact for 24 h under static conditions at 20°C, while the remaining reaction mixtures were incubated for 7 days under either static or aerated conditions. After these periods, an evaluation of the waste's toxicity and biodegradability was obtained. Chemical and physical parameters of the different waste forms were also determined.

It was found that the microbes were capable of degrading the concentrated FHA Wash resulting in both a reduction in oxygen demand and toxicity. A similar pattern was displayed with the dilute FHA waste which was enhanced by a large and active contaminant population, presumably present in the neutralization pond. Further beneficial effects were obtained after prolonged contact time and a continuous aeration treatment. Comparison between summer and winter performance showed microbial activity to be superior in the former case. Chemical and physical properties of the concentrated waste rendered it unacceptable for direct disposal, however, dilution, rather than stratification, within a neutralization pond resulted in an

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improvement in wastewater quality. The concentration of six heavy metals, plus aluminum, total suspended and dissolved solids were greater than the Ontario Ministry of the Environment water quality objectives. A suggested disposal strategy is to use the neutralization pond as a storage, treatment and mixing zone, where the waste can be kept for approximately 7 months including a summer period, diluted further by 1:100 and aerated. Although this procedure will reduce all biological and chemical parameters to below regulatory limits the existence of mercury is problematic because of its ability to bioaccumulate. However, the values for mercury should be re-examined as problems were experienced with the analytical technique.

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TOXICITY AND BIODEGRADABILITY OF DARLINGTON FEEDER HEADER ASSEMBLY CLEANING WASTES

1.0 INTRODUCTION

Wastewater, from the cleaning of heavy equipment (Feeder Header Assembly - FHA) required for use at Darlington NGS, has been stored in an unused water treatment plant, waste neutralization pond at the Wesleyville GS site. This liquid waste must be disposed of without detrimentally affecting the environment into which it is discharged. A potential discharge site is the sewage lagoons at Wesleyville GS. The waste must not kill the microbial populations associated with the sewage, as they are primarily responsible for the breakdown of organic compounds and hence essential for purification processes in the lagoons. An assessment of the toxicity of concentrated FHA Wash to a winter population of sewage lagoon micro-organisms was performed in the laboratory under conditions simulating a winter situation (4°C). The biodegradability of the concentrated FHA Wash was also determined and the results presented in a report (Ontario Hydro Research Division (OHRD) Report No. C85-21-K). One of the conclusions reached was that a summer population of microbes would potentially be more tolerant of the waste's toxicity and possess a greater capacity for degradation.

The current study is an expansion of the original work to include assessments of the performance of the summer population of microbes and the toxicity and biodegradability of diluted FHA Wash. The major aim of this second phase is to provide recommendations for the disposal of dilute FHA cleaning waste stored in a neutralization pond and future batches of concentrated FHA Wash. To do this a number of objectives must be met. These are:

Objective 1: Determine whether (i) the Wesleyville sewage lagoon contains, during the summer, a greater number of active microbes that (ii) display reduced sensitivity to the toxic effect of FHA cleaning wastes and (iii) a greater capacity to biodegrade the waste than was observed for the winter population.

Objective 2: Determine whether storage of diluted FHA cleaning waste in Wesleyville neutralization ponds, open to the atmosphere, has changed the waste such that it has become less toxic/more biodegradable than the concentrated waste stored in a closed system.

Objective 3: Determine whether aeration of both concentrated and diluted FHA Wash for 7 days at 20°C will increase the biodegradability and decrease the toxicity of the wastes.

Objective 4: Determine whether there is chemical stratification of the waste during storage in the Wesleyville GS neutralization pond, and if there is a difference between the chemical composition of the concentrated FHA Wash stored in a closed vessel and the waste diluted and stored in a neutralization pond.

Objective 5: Determine a suitable method for disposing of the dilute FHA Wash, stored in the water treatment plant waste neutralization pond, the future batches of concentrated FHA cleaning wastes.

The approach taken to this study followed a similar framework to that of the previous investigation (OHRD Report No. C85-21-K).

2.0 METHODS

The three components of the experimental system were sewage sludge collected from the Wesleyville lagoon, concentrated FHA Wash that had been stored in a glass vessel and held at approximately 20°C in the laboratory for 8 months, and diluted FHA Wash taken from a neutralization pond at Wesleyville. Due to possible waste settling and collection of rain water in the neutralization pond the diluted FHA Wash was treated as three separate samples. The upper layer was taken from the top 15 cm of liquid waste, the lower layer was sampled by dragging a bottle along the bottom of the pond and the third sample contained waste that had been mixed prior to collection. All three sub samples were submitted for chemical analysis, those for heavy metal analysis were collected straight into acid washed bottles containing Ultrex pure nitric acid as a preservative. Only the mixed layer, referred to as dilute FHA Wash, underwent microbiological analysis. The concentrated FHA

Wash was subjected to both chemical and microbiological analyses.

To produce one set of reaction mixtures, serial dilutions of both dilute and concentrated FHA Wash samples were prepared in sterile distilled water. Then 60 mL of diluted chemical waste was combined with 540 mL of sewage sludge to give final concentrations of FHA Wash ranging from 5×10^{-1} to 1×10^{-5} v/v. To meet objectives 1, 2 and 3, three sets of these dilution series were held at 20°C. Two sets remained stagnant, with one sampled after 24 hours contact of FHA Wash with sewage sludge and the other after a 7 day contact period. The third set was aerated over a 7 day contact period. The controls consisted of 600 mL of sewage sludge alone, which were subjected to the previously described treatments.

After the defined reaction times the dilution series were subjected to two biological analyses. From numbers of surviving microbes, cultured at 20°C on a nutrient medium designed to support growth of the widest range of organisms possible, an assessment of the waste's toxicity was obtained. At the same time samples were sent to the Analytical Services Section for Biochemical Oxygen Demand (BOD_5) determinations using a standard procedure in which the samples are incubated for 5 days at 20°C (American Public Health Association, 1981, Part 507). The only modification to this procedure was that the samples were not seeded with another microbial inoculum because the aim of this work was to assess the degradative capacity of the Wesleyville sewage lagoon microbial population only. Also, an unexpected depression in BOD_5 values may be used as an indication of toxicity. However, because toxic levels were diluted to ensure that a BOD_5 result could be obtained, use of this method to assess toxicity is not appropriate for this study.

In order to compare BOD_5 results for concentrated and dilute FHA Wash manipulation of the dilute waste values was necessary to compensate for the dilution effect. The extent of waste dilution is not known exactly. Measurement of the volume of standing water present in the pond prior to FHA Wash addition and calculation of wastewater volume produced a dilution factor of 1:72. This is probably an over estimate of the extent of dilution because none of the chemical components of the concentrated FHA Wash showed such extensive dilution (Table 4). A 1:28 dilution level was obtained for total dissolved solids and total organic carbon, components which are good indicators of the dilution effect due to their homogeneous distribution throughout the wastewater layers. The greatest dilution recorded for any chemical component was 1:40 for zinc and lead (Table 4) and therefore, as a conservative estimate of the dilution effect, a factor of 1:40 was selected. Then a standard

curve of BOD_5 values versus apparent dilution level was drawn and used to derive BOD_5 values for the dilute waste where the dilution effect had been taken into account.

Chemical analyses performed were those listed in OHRD Report No. CE84-2389-K, that is quantification of the elements: calcium, magnesium, sodium, potassium, iron, chromium, aluminum, manganese, zinc, silver, beryllium, lead, cadmium, copper, nickel, arsenic, selenium and mercury. Due to sample handling problems for the mercury analysis, percent recovery was checked using spiked samples, and in fact 100% recovery was achieved. In addition, pH, turbidity, total suspended and dissolved solids, plus total organic carbon and alkalinity values were recorded.

3.0 RESULTS AND DISCUSSION

3.1 Biological Analyses

3.1.1 Lagoon Microbial Population Size (Objective 1, i)

The results for microbial numbers and BOD_5 as affected by concentrated and dilute FHA Wash after 24 hours contact with sewage sludge under static conditions are given in Table 1. Comparison between the initial microbial numbers in the sewage lagoon in the summer (control = 2.7×10^2 cells/mL) versus the winter value (3.7×10^3 - see Appendix A) reveals that the population is smaller in the summer than in the winter. This unexpected result may be partially explained by the thunderstorm which immediately preceeded collection of the summer samples. The heavy rainfall may have upset the population equilibrium and caused a dilution effect. Over the test period the control values did increase up to 1.3 to 1.5 $\times 10^3$ cells/mL after 7 days incubation at 20°C and even higher in the aerated controls (1.7 to 2.1 $\times 10^3$ cells/mL).

3.1.2 Toxicity of Concentrated FHA Wash (Objective 1, ii)

Before discussing the relative levels of toxicity and biodegradability of the wastes to winter and summer lagoon populations it is interesting to note that the concentrated FHA Wash at a concentration of 1×10^{-3} v/v had a BOD_5 value of 24 mg/L in the winter (see Appendix A) and 26 mg/L in the summer (Table 1). As the oxygen demand has not changed it can be assumed that the concentrated FHA Wash underwent little microbial alteration during storage in a closed glass vessel and hence comparisons between winter and summer tests are reasonable.

TABLE 1

TOXICITY AND BIODEGRADABILITY OF FHA WASH
AFTER 24 HOURS CONTACT WITH SEWAGE LAGOON BACTERIA AT 20°C

FHA Wash - Concentrated		FHA Wash Concentration in Sewage Sludge (v/v)	FHA Wash - From Neutralization Pond		
Viable Microbial Numbers (cells/mL)	Biochemical Oxygen Demand (mg/L)		Viable Microbial Numbers (cells/mL)	Biochemical Oxygen Demand (mg/L) Experimentally Derived	Biochemical Oxygen Demand (mg/L) Modified by a Dilution Factor*
2.7×10^2	4	0	2.7×10^2	<2	ND
6.0×10^2	3	1×10^{-5}	2.4×10^2	2	ND
3.2×10^3	5	1×10^{-4}	2.8×10^2	2	ND
3.4×10^3	20	5×10^{-4}	1.9×10^2	2	ND
3.0×10^3	26	1×10^{-3}	4.5×10^2	2	16
5.5×10^3	234	5×10^{-3}	1.7×10^3	2	144
1.7×10^3	570	1×10^{-2}	1.2×10^4	6	267
4.8×10^2	2500	5×10^{-2}	7.2×10^4	16	550
1.3×10^2	>3000	1×10^{-1}	9.8×10^4	23	672
22.0	>2000	5×10^{-1}	4.9×10^5	310	ND

* BOD_5 value derived from a standard curve to account for the 1:40 dilution factor.
ND - not determined.

An assessment of concentrated FHA Wash toxicity at a level of 1×10^{-3} v/v reveals that 3.2×10^{3} cells/mL, or 86% of the initial number of microbes, survived in the winter tests (Appendix A), as opposed to 3.0×10^{3} cells/mL or 110% of the control population in the summer study (Table 1). The difference is more marked at a greater FHA Wash concentration (5×10^{-3} v/v) with winter microbial values of 2.8×10^{3} cells/mL (77% survival) versus 5.5×10^{3} cells/mL in the summer (200% survival). A toxic effect for the summer population was observed at a FHA concentration of 1×10^{-2} v/v, an order of magnitude higher than the first signs of toxicity observed in the winter study (1×10^{-3} v/v). These results indicate two things. Firstly, that the summer population, although originally smaller than the winter one, is more resistant to the concentrated cleaning waste's toxicity.

Secondly, the composition of the lagoon population has changed between winter and summer. The FHA Wash stimulates growth of some of the organisms in the summer population such that an increase in FHA Wash concentration results in an increase in microbial numbers, up to a point. Further evidence for the adaption of the summer population to utilize the cleaning waste as a nutrient source can be seen when the 24-hour static values (Table 1) are compared to the 7-day static results for concentrated waste (Table 2). At an FHA Wash concentration of 1×10^{-3} v/v the number of microbes has risen from 3.0×10^{3} cells/mL to 1.3×10^{6} cells/mL after 7 days incubation at 20°C.

3.1.3 Biodegradability of Concentrated FHA Wash (Objective 1, iii)

The capacity of FHA Wash to support microbial growth is borne out by the BOD_5 results during the assessment of biodegradability. The oxygen demand for the concentrated FHA Wash (5×10^{-3} v/v) was 234 mg/L after the 24 hour exposure period plus 5 days incubation during the BOD_5 procedure (Table 1), but this had been reduced to 137 mg/L after a further 7-day contact (Table 2). Similarly, reductions in BOD_5 values were observed after 7 days for the 1×10^{-2} v/v and 5×10^{-2} v/v levels of concentrated FHA Wash. Therefore, the summer population is capable of degrading concentrated FHA Wash held at 20°C over a 7-day period. A direct comparison of BOD_5 values for summer tests (Tables 1 and 2) and the winter test (Table 1 - Appendix A) is not possible as there was insufficient dilution of the chemical in the winter, where the >51 mg/L value (Appendix A) could mean that the actual level was 60 or 6000 mg/L. However, neither static nor aerated incubation of the winter population with FHA Wash for 7 days at 4°C resulted

TABLE 2

COMPARISON BETWEEN STATIC AND AERATED SUSPENSIONS OF LAGOON BACTERIA AND CONCENTRATED FHA WASH AFTER 7 DAYS CONTACT AT 20°C

Static		FHA Wash Concentration in Sewage Sludge (v/v)	Aerated	
Viable Microbial Numbers (cells/mL)	Biochemical Oxygen Demand (mg/L)		Viable Microbial Numbers (cells/mL)	Biochemical Oxygen Demand (mg/L)
1.3×10^3	2	0	1.7×10^3	>18
1.4×10^4	1	1×10^{-5}	1.0×10^4	16
1.6×10^4	3	1×10^{-4}	1.1×10^4	16
3.4×10^5	17	5×10^{-4}	8.6×10^5	75
1.3×10^6	24	1×10^{-3}	1.1×10^6	77
8.1×10^5	137	5×10^{-3}	9.8×10^5	150
7.6×10^5	314	1×10^{-2}	1.2×10^6	110
2.2×10^5	1600	5×10^{-2}	7.3×10^5	420
2.2×10^5	1700	1×10^{-1}	2.6×10^5	1000
1.5×10^3	>4000	5×10^{-1}	1.4×10^4	5200

in waste degradation (OHRD Report C85-21-K), which leads to the conclusion that a greater degradation capacity is exhibited by the summer population.

3.1.4 Effects of Storage on Biodegradability and Toxicity of FHA Wash (Objective 2)

To determine the effects of storage upon FHA Wash the data in Table 1 must be examined. Before a direct comparison can be made for BOD_5 values (biodegradability) between concentrated and dilute FHA Wash samples, the effect of dilution on the waste stored in the neutralization pond must be determined. As described in the methods, a dilution factor of 1:40 was selected. Because the relationship between concentration of dilute waste and BOD_5 is not directly proportional, straight multiplication of the BOD_5 value was not possible. Hence, a standard curve of BOD_5 versus apparent dilution level was used to derive the values shown in Table 1. Even when the dilution effect has been take into account, it can be seen that these BOD_5 values for dilute waste are considerably different to those for concentrated FHA Wash. For example, at the 5×10^{-3} v/v level, the result for dilute waste is 144 mg/L versus 234 mg/L for concentrated waste. Therefore, it is concluded that there was a decrease in biochemical oxygen demand greater than would have resulted from a dilution effect alone.

To determine if there has been any change in waste toxicity with storage, microbial numbers for concentrated and dilute waste must be compared. The approach described previously to compensate for the dilution factor cannot be taken because the relationship between waste concentration and individual numbers is not consistent throughout the dilution series. Examination of the microbial count for concentrated FHA Wash reveals an increase in numbers above the control value at the higher waste dilutions followed by a gradual decline in numbers as the concentration increases. This pattern is attributed to stimulation of the sewage sludge population as the FHA Wash is utilized to support growth during the 24 hour period until the concentration of chemical waste is such that toxicity and hence inhibition occurs. Therefore, although it is expected that there would be a difference between concentrated and dilute FHA Wash microbial populations due to dilution, the extent of that difference is not known.

There is a marked change in the relationship between microbial numbers in the sewage sludge and dilute FHA Wash concentration. The population remained similar to that in the control up to a level of 1×10^{-3} v/v and then gradually increased with increasing dilute waste concentration such that the greatest number of organisms attained, 4.9×10^5 cells/mL, was orders of

magnitude greater than the control. The BOD_5 values follow a similar trend, with consistently low levels up to a concentration of 5×10^{-3} v/v followed by an increase. This link between microbial numbers and BOD_5 values lends support to the supposition that some of the population increase in a result of FHA Wash degradation/utilization as a nutrient source. However, it is unlikely that such a population size would be obtained due to waste biodegradation/growth stimulation within the 24 hour incubation period only. The putrid smell observed during collection suggests biological activity and cell death. It seems that the dilute waste in the neutralization pond is contaminated with an additional population of naturally occurring micro-organisms, which would explain the concommitant rise in microbial numbers with increasing FHA Wash concentration. The low microbial numbers/BOD_5 values at the greater dilution levels of FHA Wash are probably caused by insufficent chemical to support enhanced growth and over dilution of the "contaminant" population. The existence of this "contaminant" population would help explain the low BOD_5 values observed for the dilute waste over and above a straight dilution effect.

In summary, the dilute FHA Wash contains a population of microbes that may have arisen as a result of aerial contamination or from human waste added to the pond. During storage this population has degraded the waste so that microbial numbers have risen and biochemical oxygen demand declined by a factor greater than would have been expected to be brought about by a dilution effect alone. The net result of storage of concentrated FHA Wash in a neutralization pond has been to reduced its toxicity and increase its biodegradability.

3.1.5 Effects of Prolonged Incubation at 20°C Under Static or Aerated Conditions Upon Waste Quality (Objective 3)

Assessment of the effect of aeration upon toxicity and biodegradability of the wastes is based upon the results presented in Table 2 for concentrated FHA Wash and Table 3 for the dilute waste. For the concentrated waste, the reaction mixture maintained under a static regime for 7 days showed stimulation of microbial growth up to the 1×10^{-3} v/v level, and then a toxic effect at 5×10^{-3} v/v that increased with increasing waste concentration. However, the population size was sufficiently large that even at 5×10^{-1} v/v the toxicity was not great enough to reduce the numbers to below the control value. A similar pattern was found for the aerated waste, except that the toxic effect was not evident until the 5×10^{-2} v/v level, and the population in contact with the highest FHA Wash concentration remained greater than the control. Therefore, the toxicity of the concentrated waste was reduced by

the aeration process.

Table 2 shows that aeration also resulted in decreased BOD_5 values at the higher concentrations of cleaning waste (1×10^{-2} v/v and greater). The lower oxygen demand may be due to either enhanced waste breakdown by microbes or possibly loss of a volatile toxic component, thereby reducing the inhibitory effect. Aeration could have improved waste degradation by increasing cell to nutrient/waste contact. However, the trend is reversed at a dilution of 5×10^{-3} v/v and below, where unexpectedly elevated BOD_5 values were obtained. This result, also observed for the aerated versus static control, may be partially due to heightened respiration of microbes using nutrients from the sewage sludge which resulted in oxygen consumption, in addition to oxygen utilization for waste breakdown. Determination of BOD_5 values is such that oxygen consumption by any biochemical process is recorded, with no differentiation between multiple processes that may be involved. However, the major contributor to elevated BOD_5 values may be the aeration process itself. BOD_5 values are calculated from the difference between initial and final dissolved oxygen levels. If the initial value is artificially high due to direct introduction of oxygen to wastewater by aeration, then it follows that loss of gases by diffusion during sample handling and measurement will result in a greater difference between initial and final dissolved oxygen levels.

It is concluded that decreased toxicity is a result of microbial breakdown of waste, which in turn is demonstrated by the lower biochemical oxygen demand. This trend can be seen for the concentrated waste between 24-hour static test results (Table 1) and the lower BOD_5 values for the 7-day static waste (Table 2). This trend was also evident for the higher concentrations of FHA Wash which underwent an aeration treatment (Table 2), indicating that aeration appears to increase biodegradation and reduce toxicity.

Consideration of Table 3 reveals the toxicity/biodegradability effects for the dilute FHA Wash collected from a neutralization pond. Numbers of bacteria increased with increasing dilute FHA concentration for static and aerated systems, but with aeration stimulating more growth. The gradual rise in microbial numbers with increasing waste concentration is not unexpected, assuming that there is a contaminant microbial population, because a dilution series will alter both the chemical and biological content of the reaction mixture. There is an indication of a toxic effect at the highest waste concentration. On the basis that the contaminant population should follow a dilution series approximately, the value of 3.9×10^6 cells/mL at the 1×10^{-1}

v/v dilution level should be five times greater at 5×10^{-1} v/v. That is, the number theoretically should be 1.95×10^{7} cells/mL instead of the experimentally derived result of 5.5×10^{6} cells/mL.

The reduction in BOD_5 values was less consistent for the static and aerated tests so that the improvement in sample quality with length of incubation and aeration was only clear at the 5×10^{-1} v/v level. The confounding effect of elevated BOD_5 values for both static and aerated 7-day tests as compared to the 24-hour test (Table 1) is again attributed to a combination of heightened respiration concurrent with the observed increase in biomass, and the direct effect of aeration upon dissolved oxygen values. It is to be expected that this phenomenon would be more marked for dilute FHA Wash than concentrated Wash due to the presence of a contaminant microbial population. Therefore, the effects which cause elevated BOD_5 values overlap with the trend of decreased oxygen demand resulting from waste breakdown, so that the latter process is only apparent at the highest waste concentration. In summary, the enhancement of degradation for concentrated and dilute FHA wastes may be a function of both increased microbial respiration due to higher oxygen levels and improved microbial cell-chemical contact through thorough mixing of the reactants, much along the lines of optimized activated sludge digesters used in waste treatment plants.

It can be concluded that incubation of sewage sludge with both dilute and concentrated FHA Wash at 20°C for 7 days under static conditions decreased the waste's toxic effect. A further reduction in toxicity, manifested by a rise in microbial numbers, was obtained after an aeration treatment. The impact of prolonged incubation at 20°C and aeration was less clear with respect to waste biodegradability because in some cases elevated BOD_5 values, attributed to heightened respiration and direct aeration effects, were attained. However, for concentration FHA Wash (Table 2) it was concluded that incubation and aeration resulted in greater biodegradation. For the dilute waste a reduction in BOD_5 was only apparent at the highest waste concentration, although this level most closely represents the real life situation/waste concentration. Alternatively, it could be argued that the minimal improvement in dilute waste quality was not sufficient to warrant an aeration treatment.

3.2 Chemical Analyses (Objective 4)

Criteria for discharge of industrial wastes include chemical characteristics as well as toxicity and biodegradability. Chemical analyses were carried out on the different layers of dilute waste taken from the neutralization pond on the concentrated FHA Wash. Analysis of these layers would allow

TABLE 3

COMPARISON BETWEEN STATIC AND AERATED SUSPENSIONS OF LAGOON BACTERIA AND DILUTE FHA WASH FROM A NEUTRALIZATION POND AFTER 7 DAYS CONTACT AT 20°C

Static		FHA Wash Concentration in Sewage Sludge (v/v)	Aerated	
Viable Microbial Numbers (cells/mL)	Biochemical Oxygen Demand (mg/L)		Viable Microbial Numbers (cells/mL)	Biochemical Oxygen Demand (mg/L)
1.5×10^3	1	0	2.1×10^3	>19
1.2×10^3	1	1×10^{-5}	1.8×10^3	>7
1.7×10^3	1	1×10^{-4}	2.3×10^3	>7
1.2×10^3	1	5×10^{-4}	1.8×10^3	>7
1.4×10^3	1	1×10^{-3}	1.6×10^3	>18
3.6×10^3	2	5×10^{-3}	1.5×10^4	>18
1.1×10^4	3	1×10^{-2}	4.2×10^4	17
1.4×10^5	18	5×10^{-2}	7.8×10^5	87
5.2×10^5	44	1×10^{-1}	3.9×10^6	60
1.7×10^6	222	5×10^{-1}	5.5×10^6	160

determination of whether chemical stratification of the waste had occurred during storage, and whether there was a difference in chemical composition between concentration waste and FHA Wash diluted and stored in a neutralization pond.

In Table 4 the data are compared with the allowable effluent concentrations specified in the Provincial Water Quality Objectives (Ontario Ministry of the Environment, 1984), and with previous analyses of standing water present in the neutralization pond prior to FHA Wash addition (OHRD Report No. (CE84-2389-K).

As expected, the effect of dilution on the waste is marked when concentrations for the mixed waste from the neutralization pond are compared to the concentrated waste that was stored in the laboratory in a sealed glass vessel (Table 4). With the exception of pH, which is at the upper acceptable limit, all the constituents of the concentrated FHA Wash are in excess of Ontario Ministry of Environment guidelines and therefore the concentrated waste is not suitable for discharge to the lagoon in its unmodified state. However, dilution of the FHA cleaning waste when it was added to standing water in an open neutralization pond resulted in reduced concentrations for heavy metals and physical parameters, many to the extent that recommended Provincial objectives were not exceeded. As previously discussed in section 3.1.4, the extent of dilution is not clear. This is indicated by the ratio of diluted to concentrated FHA Wash shown in Table 4, which ranges from 1:0.6 for potassium up to 1:40 for zinc and lead. This variation in apparent dilution level may be caused by other processes, such as complexation followed by precipitation of elements, thereby removing them from solution and hence increasing the "dilution effect". Heavy metals in particular would be prone to such processes, and indeed zinc and lead do show extensive "dilution". It is concluded that dilution of the concentrated waste, by storage in a neutralization pond containing standing water, resulted in a beneficial alteration in waste quality.

The second part of the objective was to ascertain if stratification of the dilute waste in the neutralization pond had taken place. Comparison of concentrations of elements in the upper and lower layers reveals that only slight stratification has occurred. In regard to a disposal strategy, it does not appear feasible to drain off the supernatent and treat the bottom sludge layer separately because where concentrations of heavy metals exceed Provincial water quality objectives the reduction in concentration due to formation of separate layers is minimal. Therefore, dilution of FHA Wash in

TABLE 4

CHEMICAL ANALYSES OF VARIOUS FORMS OF FHA WASH

Analyte (mg/L)*	FHA Wash From Neutralization Pond			Concentrated FHA Wash	Ratio of Diluted to Concentrated FHA Wash	OMOE Water Quality Objectives (mg/L)	Ratio of Diluted Waste to OMOE Water Quality Objectives
	Undisturbed Upper Layer	Undisturbed Lower Layer	Upper and Lower Layers - Mixed				
pH	6.9	6.8	6.9	9.4		6.5-8.5	
Turbidity NTU	110.	125.	110.	200.	1:2		
Total Alkalinity as mg $CaCO_3$/L	157.	181.	160.	3000.	1:19		
Total Suspended Solids	56.	180.	120.	380.	1:3		
Total Dissolved Solids	930.	910.	910.	24,200.	1:27		
Total Organic Carbon	580.	550.	550.	15,600.	1:28		
Calcium	34.	51.8	38.3	204.	1:5		
Magnesium	3.08	4.18	3.31	15.8	1:5		
Sodium	48.4	48.2	49.0	774.	1:16		
Potassium	15.3	15.3	14.8	8.4	1:0.6		
Iron	0.95	1.48	1.12	17.3	1:15	0.3	37:1
Chromium	<0.1	<0.1	<0.1	0.8	1:8	0.1	<1:1
Aluminum	<1.0	<1.0	<1.0	4.8	1:5	0.1	<10:1
Manganese	0.127	0.139	0.133	3.27	1:26		
Zinc	0.107	0.152	0.158	6.35	1:40	0.03	5:1
Silver	<0.0002	<0.0002	<0.0002	0.001	1:5	0.0001	<2:1
Beryllium	<0.0002	<0.0002	<0.0002	0.0005	1:3	1.1	0.0002:1
Lead	0.021	0.024	0.024	0.97	1:40	0.025	1:1
Cadmium	0.0007	0.0008	0.0007	0.0036	1:5	0.0002	3.5:1
Copper	0.040	0.058	0.051	1.23	1:24	0.005	10:1
Nickel	0.005	0.005	0.005	0.068	1:14	0.025	0.2:1
Arsenic	<0.001	<0.001	<0.001	0.012	1:15	0.1	<0.01:1
Selenium	<0.001	<0.001	<0.001	<0.001	1:1	0.1	<0.01:1
Mercury	0.002†	0.009†	0.009†	0.002†	5:1	0.0002	45:1

* = total concentration, sample not filtered. Applies to all analytes except mercury.
† = sample filtered prior to analysis.

separate layers is minimal. Therefore, dilution of FHA Wash in the neutralization pond is the critical factor in attaining concentrations acceptable for disposal, not stratification.

Examination of Table 4 shows that concentrations of many of the physical parameters and elements in the dilute FHA Wash will not present a disposal problem, however, in some cases OMOE guidelines are exceeded (OMOE, 1984). These elements are iron, aluminum, zinc, silver, cadmium, copper and mercury, which exceed Provincial guidelines both in the mixed waste and in the upper layer. The extent of dilution necessary to reduce these elements to acceptable levels is small, as can be seen in the final column of Table 4, for all cases except mercury. Physical parameters such as suspended solids are not listed in the Provincial Water Quality Objectives, but OMOE frequently specifies a discharge limit of 15 mg/L above the background level. The measured concentration of 120 mg/L suspended solids exceeds the ambient, which is estimated to be 10 mg/L, by 110 mg/L. A precise value for dissolved solids is not given by the Ministry of the Environment, but the value for the dilute FHA Wash is high. All of the above values would be reduced by several orders of magnitude if the wastes were to be added to the Wesleyville sewage lagoons, lowering them to below the Provincial Water Quality Objectives such that they should be acceptable for discharge to Lake Ontario.

The one element of concern is mercury. Provincial guidelines stipulate a limit of 0.2 µg/L for existing discharges and a limit of zero for new sources. The results for this element are confusing as it appears that the concentrated waste contains less mercury than the dilute waste. Problems with sample analysis were encountered due to the high organic content. However, the value for mixed dilute waste of 9 µg/L is in excess of the OMOE Guidelines. The mercury concentration can be reduced through dilution, but whether this would be acceptable for an element which bio-accumulates is dependent upon OMOE review of this specific case.

It is concluded that there was a difference between concentrated and diluted waste stored in a neutralization pond. Much of the change was attributed to dilution, with some alteration caused by heavy metal complexation and precipitation. Partial stratification of the dilute waste had occurred, but not to the extent that different layers could be disposed of separately, The relatively high concentration of mercury may present a disposal problem.

3.3 Disposal Strategy (Objective 5)

An acceptable disposal strategy must combine biological and chemical needs. From a biological standpoint, none of the tests

revealed an unacceptable level of toxicity towards the summer microbial population, with the exception of the concentrated FHA Wash 24-hour contact test where 92% cell death occurred at the 5×10^{-1} v/v level. The evaluation of biodegradability was based on BOD_5 values and although the Provincial water quality objectives do not cite this parameter, it is mentioned in a document covering the discharge of industrial effluents as being limited to 15 mg/L BOD_5 (Ontario Ministry of the Environment, 1974). BOD_5 values for the least dilute sample of both concentrated and diluted waste, which is closest to the real life situation, followed a progressive decline with increased incubation period at 20°C and with aeration; although this trend between treatments was unclear for greater dilutions because of effects previously described that were associated with aeration. The degree of dilution to reduce BOD_5 values to an acceptable level would be excessive for concentrated waste, but for dilute waste would be 1:20 for 24-hr and 7-day static systems or 1:100 for the 7-day aerated treatment.

Dilution alone is not sufficient treatment. It was demonstrated that prolonged incubation of a winter population of sewage lagoon microbes with concentrated FHA Wash at 4°C under both static and aerated regimes did not result in an improvement in biodegradability (OHRD Report No. C85-21-K). In contrast, decreased toxicity and increased biodegradability were obtained in this study when a summer population of sewage lagoon microbes and neutralization pond contaminant organisms were tested. Therefore, it is recommended that the cleaning waste be held for approximately six months, which should include the summer months when the microbial populations are at their most active and hence capable of drastically reducing the biochemical oxygen demand. The requirement for aeration is less clear but, because improvement in waste quality was obtained with the most concentrated level of dilute FHA Wash, it is still suggested as a worthwhile treatment.

From a chemical standpoint, all of the elements which exceed Provincial guidelines would not do so if the dilute FHA Wash that was stored in a neutralization pond was further diluted by 1:100. The dilution level is the conservation estimate for BOD_5 requirements derived for dilute waste which had been aerated. Although mercury requires a 1:45 dilution to meet concentration criteria there is still the aspect of bio-accumulation to be considered. However, it is anticipated that discharges from the neutralization pond would be infrequent and that the total amount of concentrated FHA Wash to be dealt with will be approximately 116,378 litres. Provincial guidelines indicate that industrial effluents requiring discharge are dealt with on a case by case basis and cite the potential for mixing zones, although the mode of application is not well defined. It would

appear to be feasible to use the neutralization pond as a storage and treatment "mixing zone", so that the quality of the FHA Wash can be brought to acceptable levels prior to discharge to the lake via the sewage lagoon. An alternative disposal strategy would be to use chemical agents to precipitate the suspended heavy metals. Then the supernatent could be siphoned off to the sewage lagoon and the lower sludge layer disposed of separately.

4.0 CONCLUSIONS AND RECOMMENDATIONS

1. The initial number of microbes collected from the sewage lagoon in the summer months was less than that found in the winter.

2. However, the summer microbial population was more resistant to concentrated FHA Wash than the winter population as at 20°C a toxic effect was not detected until the 1×10^{-2} v/v level, or order of magnitude greater than that observed for the test carried out at 4°C.

3. Low levels of concentrated cleaning waste stimulated microbial growth. This indicated a change in composition of the sewage lagoon population since the winter because some microbes could utilize the waste as a nutrient.

4. The biochemical oxygen demand of the concentrated waste was reduced after contact with sewage lagoon micro-organisms held at 20°C for 7 days, which had not been observed for the winter investigation. It was concluded that a greater degradative capacity was exhibited by the summer lagoon population.

5. The toxicity data, revealed that storage and dilution of concentrated FHA waste in a neutralization pond resulted in decreased toxicity.

6. The dilute FHA Wash was discovered to have been contaminated by a large microbial population which drastically reduced the BOD_5 level, thereby improving the quality of the waste. This activity in combination with decreased toxicity resulted in a waste that was more amenable to biodegradation than concentrated FHA Wash. Therefore, these aspects of waste quality are improved by storage of the waste over the summer months when the microbes are most active.

7. Reduction of toxicity and increased biodegradation observed for the concentrated waste over a 7-day contact period were both enhanced by the aeration process.

8. Continuous aeration of dilute FHA Wash for 7 days was found to stimulate microbial growth which caused decreased toxicity and increased degradation of the waste at the most concentrated level, which is closest to the actual concentration in the neutralization pond. On this basis it appears that an aeration treatment of the waste could be beneficial.

9. All the values for physical and chemical parameters for the concentrated waste, except for pH, were in excess of Ontario Ministry of the Environment guidelines, whereas many of these levels had been reduced through dilution of the waste in the neutralization pond.

10. Stratification of dilute waste in the neutralization pond had occurred, but the difference in concentration of chemical constituents between layers was not sufficient to allow separate disposal of the supernatent and bottom sludge layers. Therefore, dilution and storage of FHA Wash in a neutralization pond are the critical factors in approaching disposal, not stratification.

11. The concentrations of iron, aluminum, zinc, silver, cadmium, copper, mercury, suspended and dissolved solids in the dilute FHA Wash exceeded Provincial guidelines. Use of a neutralization pond as a "mixing zone" and dilution by a factor of 1:100 will reduce both chemical and biological parameters to acceptable levels. The only exception is mercury, which is of concern because of its ability to concentrate through the food chain. The Ministry of the Environment specify zero discharge for new mercury sources. However, the low mercury concentration, less than Provincial water quality objectives after a 1:100 dilution, and the one time nature of the proposed discharge may make disposal of the waste to the lake acceptable. Furthermore, the validity of the mercury values is questionable because of the problems experienced during chemical analysis.

To ensure that disposal of concentrated FHA Wash meets with Ontario Ministry of the Environment guidelines it is recommended that the waste be diluted by a factor of at least 1:40 and stored for a period of approximately 7 months in a neutralization pond at the Wesleyville site. This period should encompass the summer months when microbial degradative activity is at a maximum. Further improvement of waste quality must be

achieved by additional dilution (1:100) of the waste and combined with an aeration treatment if possible. Dilution of the existing dilute FHA Wash should bring the waste to acceptable levels for discharge, although discussion with the regulatory agency is required.

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APPENDIX A

DATA FOR THE TOXICITY AND BIODEGRADABILITY OF FHA WASH UNDER WINTER CONDITIONS*

TABLE 1

FHA Wash Concentration in Sewage Sludge (v/v)	Viable Microbial Numbers (Cells/mL)	Percentage Surviving Bacteria	Biochemical Oxygen Demand$_5$ (mg/L) Contact Period With FHA Wash		
			24 hours	7 days	
			Static	Static	Aerated
0	3.7×10^3	100	<1		
1×10^{-5}	4.2×10^3	>100	3		
1×10^{-4}	3.7×10^3	100	3		
5×10^{-4}	4.1×10^3	>100	12		
1×10^{-3}	3.2×10^3	86	24	23	29
5×10^{-3}	2.8×10^3	77	>51		
1×10^{-2}	1.7×10^3	47	>56		
5×10^{-2}	3.2×10^2	9	>50		
1×10^{-1}	2.0×10^1	<1	>49		
5×10^{-1}	0	0	3		

* Taken from OHRD Report No. C85-21-K.